

CLAIMS

1. A process in two steps for the preparation of 1-octene starting from butadiene which comprises:

5 ** a first step (a) in which the bis-hydrodimerization of butadiene to 1,7-octadiene is effected in the presence of a catalyst based on palladium containing one or more tri-substituted monodentate phosphines, the molar ratio palladium/phosphines ranging from 3 to 50, in an aprotic polar
10 solvent optionally containing an organic base; the above first step being carried out in the presence of a hydrogen donor;

** a second step (b) in which the partial catalytic hydrogenation of 1,7-octadiene, recovered at the end of the
15 first step, to 1-octene, is effected; the above hydrogenation being carried out under hydrogen pressure or mixtures of hydrogen and nitrogen, in the presence of a catalyst;
the above process being characterized in that in step (b)
20 the catalyst is selected from titanium compounds in the presence of activators selected from one or more metal alkyls of group 13.

2. The process according to claim 1, wherein in the first step, the molar ratio palladium/phosphine ranges from 3 to 50, preferably from 5 to 30.

25 3. The process according to claim 1, wherein in the first

step, the hydrogen donor is formic acid.

4. The process according to claim 1, wherein the hydrogen donor is in a stoichiometric ratio of 1:2 with respect to the butadiene.

5 5. The process according to claim 1, wherein the catalyst based on palladium is selected from palladium carboxylates.

6. The process according to claim 5, wherein the palladium carboxylate is Pd(acetate)₂.

7. The process according to claim 1, wherein in the first
10 step, the aprotic polar solvent is selected from di-substituted amides and disubstituted cyclic ureas.

8. The process according to claim 7, wherein the disubstituted amide is dimethyl formamide.

9. The process according to claim 7, wherein the disubstituted cyclic ureas are selected from dimethyl ethylene urea and dimethyl propylene urea.

10. The process according to claim 1, wherein in the first step, the organic base is triethyl amine.

11. The process according to claim 1, wherein the temperature of the first step ranges from 50 to 120°C.

12. The process according to claim 11, wherein the temperature of the first step ranges from 70 to 100°C.

13. The process according to claim 1, wherein in the first step, the molar ratio between organic base and hydrogen donor ranges from 0 to 1.5.

14. The process according to claim 13, wherein the molar ratio between organic base and hydrogen donor ranges from 0.2 to 1.3.

15. The process according to claim 14, wherein the molar ratio between organic base and hydrogen donor ranges from 5 0.4 to 0.8.

16. The process according to claim 1, wherein the selective hydrogenation of 1,7-octadiene to 1-octene is carried out in the second step in the presence of a catalytic system comprising one or more catalysts selected from titanium compounds and one or more activators selected from aluminum alkyls and aluminoxanes.

17. The process according to claim 16, wherein the molar ratio between the catalyst and 1,7-octadiene ranges from 15 1/100 to 1/100,000, preferably from 1/1,000 to 1/10,000.

18. The process according to claim 16, wherein the molar ratio between the activator and catalyst ranges from 1/1 to 10,000/1, preferably from 1/1 to 2000/1.

19. The process according to claim 16, wherein the second 20 step is carried out at a temperature ranging from 0°C to 150°C, preferably from 50° to 120°C.

20. The process according to claim 16, wherein the titanium compound is selected from $Ti(OtBut)_4$, $Ti(EtO)_4$ and Cp_2TiCl_2 .

25 21. The process according to claim 16, wherein the activa-

tor is selected from MAO (methyl aluminoxane), TIBA (aluminum triisobutyl), DIBAH (diisobutyl aluminum hydride), TMA (trimethyl aluminum), TEA (triethyl aluminum).

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AMENDED CLAIMS

[received by the International Bureau on 17 March 2005 (17.03.05);
Original claims 1-2 replaced by new claims 1-2 (4 pages).]

1. A process in two steps for the preparation of 1-octene starting from butadiene which comprises:

5 ** a first step (a) in which the bis-hydrodimerization of butadiene to 1,7-octadiene is effected in the presence of a catalyst based on palladium containing one or more tri-substituted monodentate phosphines, the molar ratio palladium/phosphines ranging from 50 to 3, in an aprotic polar
10 solvent optionally containing an organic base; the above first step being carried out in the presence of a hydrogen donor;

** a second step (b) in which the partial catalytic hydrogenation of 1,7-octadiene, recovered at the end of the
15 first step, to 1-octene, is effected; the above hydrogenation being carried out under hydrogen pressure or mixtures of hydrogen and nitrogen, in the presence of a catalyst; the above process being characterized in that in step (b) the catalyst is selected from titanium compounds in the
20 presence of activators selected from one or more metal alkyls of group 13.

2. The process according to claim 1, wherein in the first step, the molar ratio palladium/phosphine ranges from 50 to 3, preferably from 30 to 5.

25 3. The process according to claim 1, wherein in the first

step, the hydrogen donor is formic acid.

4. The process according to claim 1, wherein the hydrogen donor is in a stoichiometric ratio of 1:2 with respect to the butadiene.

5 5. The process according to claim 1, wherein the catalyst based on palladium is selected from palladium carboxylates.

6. The process according to claim 5, wherein the palladium carboxylate is $\text{Pd}(\text{acetate})_2$.

7. The process according to claim 1, wherein in the first
10 step, the aprotic polar solvent is selected from disubstituted amides and disubstituted cyclic ureas.

8. The process according to claim 7, wherein the disubstituted amide is dimethyl formamide.

9. The process according to claim 7, wherein the disubstituted cyclic ureas are selected from dimethyl ethylene urea and dimethyl propylene urea.

10. The process according to claim 1, wherein in the first step, the organic base is triethyl amine.

11. The process according to claim 1, wherein the temperature of the first step ranges from 50 to 120°C.

12. The process according to claim 11, wherein the temperature of the first step ranges from 70 to 100°C.

13. The process according to claim 1, wherein in the first step, the molar ratio between organic base and hydrogen donor ranges from 0 to 1.5.

14. The process according to claim 13, wherein the molar ratio between organic base and hydrogen donor ranges from 0.2 to 1.3.

15. The process according to claim 14, wherein the molar ratio between organic base and hydrogen donor ranges from 5 0.4 to 0.8.

16. The process according to claim 1, wherein the selective hydrogenation of 1,7-octadiene to 1-octene is carried out in the second step in the presence of a catalytic system comprising one or more catalysts selected from titanium compounds and one or more activators selected from aluminum alkyls and aluminoxanes.
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17. The process according to claim 16, wherein the molar ratio between the catalyst and 1,7-octadiene ranges from 15 1/100 to 1/100,000, preferably from 1/1,000 to 1/10,000.

18. The process according to claim 16, wherein the molar ratio between the activator and catalyst ranges from 1/1 to 10,000/1, preferably from 1/1 to 2000/1.

19. The process according to claim 16, wherein the second 20 step is carried out at a temperature ranging from 0°C to 150°C, preferably from 50° to 120°C.

20. The process according to claim 16, wherein the titanium compound is selected from $Ti(OtBut)_4$, $Ti(EtO)_4$ and Cp_2TiCl_2 .

25 21. The process according to claim 16, wherein the activa-

tor is selected from MAO (methyl aluminoxane), TIBA (aluminum triisobutyl), DIBAH (diisobutyl aluminum hydride), TMA (trimethyl aluminum), TEA (triethyl aluminum).

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